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TI - METHOD FOR MOLDING AND VULCANIZING RUBBER PRODUCT
IN - HASHIMOTO TAKATSUGU;MISHIMA HISAMI
PA - BRIDGESTONE CORP
IC - B29C33/04 ; B29C33/76 ; B29C35/04 ; B29D30/00 ; B29K21/00 ;
B29K83/00 ; B29K105/24 ; B29L30/00

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TI - Moulding and vulcanisation of rubber prod. e.g. tyres - contg a vulcanising bladder with an innermost butyl rubber layer and an outer layer including e.g. a silicone rubber, etc.
PR - JP19910213237 19910731
PN - JP5031724 A 19930209 DW199311 B29C33/04 006pp
PA - (BRID) BRIDGESTONE CORP
IC - B29C33/04 ;B29C33/76 ;B29C35/04 ;B29D30/00 ;B29K21/00 ;
B29K83/00 ;B29K105/24 ;B29L30/00
AB - J05031724 In the moulding and vulcanisation of a rubber prod., using vulcanising bladder, the bladder has a multilayer structure. The innermost layer is produced from a compsn. contg., as a major ingredient, an organic rubber. The outermost layer is produced from a rubber compsn. which has a release stress for the rubber prod. below 0.5 kg/cm.
- The thickness of the innermost layer is above 0.02mm. The organic rubber is a butyl rubber.
- USE/ADVANTAGE - For tyres. The innermost layer has high steam impermeability. The bladder has excellent mechanical strength, heat resistance, steam durability, etc., and a long service life. Releasing agents are unnecessary(Dwg.0/0)

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AP - JP19910213237 19910731
IN - HASHIMOTO TAKATSUGU; others:01

- PA - BRIDGESTONE CORP
- TI - METHOD FOR MOLDING AND VULCANIZING RUBBER PRODUCT
- AB - PURPOSE: To mold and vulcanize a rubber product such as a tire with good workability without generating molding inferiority by using vulcanizing bladder excellent in mechanical properties, physical properties such as hot water resistance and chemical properties and having good durability and releasability.
- CONSTITUTION: In the molding and vulcanization of a rubber product using a vulcanizing bladder, the vulcanizing bladder is formed so as to have a multilayered structure composed of a plurality of layers and has a layer (A) composed of a rubber composition based on org. rubber on the innermost side thereof and a layer (B) composed of a rubber composition whose release stress with the rubber product is 0.5kg/cm or less on the outermost side thereof.
- SI - B29K21/00 ;B29K83/00 ;B29K105/24 ;B29L30/00
- I - B29C33/04 ;B29C33/76 ;B29C35/04 ;B29D30/00

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2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] it forms as multilayer structure which the aforementioned vulcanization bladder becomes from two or more layers in carrying out molding vulcanization of the rubber goods using a vulcanization bladder -- having -- (A) -- the molding vulcanization method of the rubber goods characterized by to have the layer which becomes the maximum inside from the rubber constituent which makes organic rubber a principal component, and to have the layer to which exfoliation stress with rubber goods becomes (B) maximum outside from the rubber constituent of 0.5 or less kg/cm

[Claim 2] The molding vulcanization method of rubber goods according to claim 1 that rubber constituent layer thickness which makes a principal component the organic rubber arranged inside [maximum] the aforementioned vulcanization bladder is characterized by being 0.02mm or more.

[Claim 3] The average thickness of the whole multilayer structure of the aforementioned vulcanization bladder is 2.0mm. The molding vulcanization method of the rubber goods according to claim 1 characterized by being above.

[Claim 4] The molding vulcanization method of rubber goods according to claim 1 that the organic rubber used for the rubber constituent layer inside [maximum] the aforementioned vulcanization bladder is characterized by being isobutylene isoprene rubber.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the molding vulcanization method using the improved vulcanization bladder of being suitable for molding vulcanization of rubber goods, especially a tire, etc.

[0002]

[Description of the Prior Art] the tire which is not cast by the vulcanization bladder which has arranged the pneumatic tire inside a non-cast tire in a molding press conventionally -- metal mold -- turning -- the method of outside -- pressing -- a non-cast tire -- metal mold -- it presses to a front face and is manufactured by carrying out molding hardening the exterior where a non-cast tire determines the structure of a tire-tread pattern and a side attachment wall by this method -- molding vulcanization is carried out to metal mold

[0003] As a constituent of the bladder for vulcanization used for molding vulcanization of rubber goods, such as such a tire, organic rubber, especially isobutylene isoprene rubber have been used conventionally. However, the vulcanization bladder which consists of organic rubber had the inclination at which a vulcanization bladder turns, when a mold-release characteristic and lubricity with a tire inside were bad and was receipts and payments of a vulcanization bladder, and it had the problem which a defective generates in molding of the tire by metal mold. Moreover, the front face of a vulcanization bladder was worn out, it became a split face, and there was a problem from which a vulcanization bladder adheres to a tire inside in vulcanization bladder contraction process in which bladder front faces are after tire hardening and a tire hardening cycle. Furthermore, since air bubbles were shut up between a vulcanization bladder and a tire front face, the heat transfer became inadequate and there was a problem which promotes a tire vulcanization defect.

[0004] In case vulcanization fabrication of a tire is performed using a vulcanization bladder, in order to solve an above-mentioned problem and to make good a mold-release characteristic with a tire inside, and lubricity, the release agent which consists of a silicone emulsion etc. was needed conventionally. However, there are not only disadvantageous points, such as increase of the increase in a man day and middle stock, from the field of a manufacturing process, but this release agent did the bad influence at the time of tire molding vulcanization, and applying a release agent to a tire inside often had it with the cause of defective generating, and the bird clapper.

[0005] How to reform mold-release characteristic lubricant conventionally as a method of solving such a problem (the 57 to 111393rd numbers of Japanese Provisional Publication No., the 57 to 111394th numbers of Japanese Provisional Publication No., Japanese Provisional Publication No. No. 119992 [57 to], the 61 to 175009th numbers of Japanese Provisional Publication No., the 62 to 275711st numbers of Japanese Provisional Publication No., the 63 to 147610th number [of Japanese Provisional Publication No.]), the method (the 59 to 106948th numbers of Japanese Provisional Publication No. --) of reforming the organic rubber front face of a vulcanization bladder with a hardening silicone film Japanese Provisional Publication No. 61-215015th A number and Japanese Provisional Publication No. 61-100417th A number, The method using the rubber mixture constituent which contains organic rubber and a polyorganosiloxane as a rubber constituent of the bladder for tire vulcanization (Japanese Provisional Publication No. No. 72505 [61 to]) Japanese Japanese Patent Application No. 61-271734th A number and Japanese Provisional Publication No.

61-175009th Number, Japanese Provisional Publication No. 63-125311st A number and Japanese Provisional Publication No. 61-195810th A number and Japanese Provisional Publication No. 61-100416th The method of using a number and a silicone rubber constituent independently etc. has been proposed.

[0006]

[Problem(s) to be Solved by the Invention] However, in use of the vulcanization bladder improved by the method enumerated upwards, the molding vulcanization method of a tire of having fully satisfied the request of the industry was not able to be offered so that it might explain below. for example, by the method which cannot acquire mold release effect sufficient by the method of reforming above-mentioned mold-release characteristic lubricant, and reforms an above-mentioned organic rubber front face with a silicone film, while the mold-release characteristic of a bladder front face and a tire inside could vulcanize the tire, without having been improved and using a release agent, the endurance of the front face of a bladder became extremely bad, and it had the problem of not being practical. While the tire could be cast without using a release agent in the method by the above-mentioned silicone rubber constituent similarly, the life as a bladder had the problem of a low extremely from the lowness of the adding-water-proof resolvability which is the fault of silicone rubber. Furthermore, while the adding-water-proof resolvability and the mechanical property which are the fault of silicone rubber were suppleable with the method by the rubber mixture constituent containing the above-mentioned organic rubber and a polyorganosiloxane with mixture of organic rubber, the mold-release characteristic of a bladder and coexistence of a bladder life had the problem of being difficult, and it was lacking in practicality. in view of the trouble of the molding vulcanization method of the conventional tire which used the above vulcanization bladders, the purpose of this invention is mechanical -- the workability which can perform molding vulcanization of rubber goods, such as a tire, is good, and it is offering the molding vulcanization method of a tire without generating of a molding defective, without excelling in a physical property and chemical property, such as a character and a hot water resistance, using the vulcanization bladder which has good endurance and a good mold-release characteristic, and using a release agent

[0007]

[Means for Solving the Problem] The purpose of this invention was attained by the molding vulcanization method of the rubber goods which have the following feature concerning this invention. with the feature, it forms as multilayer structure which the aforementioned vulcanization bladder becomes from two or more layers in carrying out molding vulcanization of the rubber goods using a vulcanization bladder -- having -- (A) -- it is having the layer which becomes the maximum inside from the rubber constituent which makes organic rubber a principal component, and having the layer to which exfoliation stress with rubber goods becomes (B) maximum outside from the rubber constituent of 0.5 or less kg/cm Here, in the molding press arranged in order of rubber goods, such as metal mold and a tire, and the vulcanization bladder from the method of outside, the maximum inside is seen from rubber goods, and means the layer of the furthest vulcanization bladder, and the maximum outside means the layer of the vulcanization bladder near rubber goods.

[0008] the average thickness of the whole multilayer structure of the vulcanization bladder used for this invention -- at least 2.0mm it is above -- required -- desirable -- 2.5mm to 50mm -- further -- desirable -- 3.0mm from -- it is 45mm the average thickness of this vulcanization bladder -- 2.0mm it is the following -- the time of rubber-goods vulcanization molding -- rubber goods -- enough -- and it is because it cannot vulcanize uniformly It is required to be at least 0.02mm or more, and the rubber constituent layer thickness which makes a principal component the organic rubber arranged inside [maximum] the vulcanization bladder used for this invention is 0.1mm still more preferably 0.05mm or more preferably. It is above. A vulcanization bladder is because the life of ** becomes it remarkably short that the organic rubber layer of this innermost layer is 0.02mm or less at the time of use, and the mechanical strengths of a rubber constituent layer run short and it destroys easily.

[0009] As organic rubber used as a principal component of the rubber constituent layer arranged at the innermost layer of the vulcanization bladder which this invention uses, setting, the rubber of diene systems, such as the rubber of saturation systems, such as isobutylene isoprene rubber, halogenation isobutylene isoprene rubber, an ethylene propylene rubber, a fluororubber, and an acrylic rubber, and natural rubber, butadiene rubber, polyisoprene rubber, chloroprene rubber,

styrene butadiene rubber, and acrylonitrile-butadiene rubber, can be used. It is rubber of a saturation system preferably and especially isobutylene isoprene rubber is desirable. It has the good dynamics physical properties at the time of an elevated temperature, and is because it excels in thermal resistance and heat-resistant aging nature.

[0010] In the above-mentioned organic rubber constituent which constitutes the rubber constituent layer of an innermost layer, the reinforcing materials described below and other additives can be added. For example, a reinforcing agent can be added in order to give only the dynamic physical properties which can be equal to use as a vulcanization bladder to this organic rubber constituent. What was chosen as this reinforcing agent from organic reinforcing agents, such as inorganic reinforcing agents, such as carbon black, white carbon, a silicic acid anhydride, a water silicic acid, a synthetic silicic acid, an activation calcium carbonate, talc, and an alumina, and high styrene resin, a cumarone indene resin, phenol resin, a lignin, denaturation melamine resin, and a petroleum resin, is used. Especially carbon black is desirable. To this organic rubber constituent, it can add altogether [for the purpose of chemicals for rubber, such as an antioxidant which is generally used in addition to the above-mentioned reinforcing agent, a heat-resistant improver, a vulcanizing agent, and a vulcanization accelerator,].

[0011] It is required for the rubber constituent layer arranged on the maximum outside of the vulcanization bladder used for this invention for ablation stress with rubber goods to use the rubber constituent of 0.5 or less kg/cm. That is because it will excel in a mold-release characteristic and the release agent application to a rubber-goods inside will become unnecessary, if ablation stress with rubber goods uses the rubber constituent of 0.5 or less kg/cm. Ablation stress uses still more preferably 0.2 or less kg/cm of rubber constituents of 0.1 or less kg/cm preferably. At least one or more sorts of constituents chosen as such a rubber constituent from the silicone rubber constituent, the mixed rubber constituent of silicone and organic rubber, the fluororubber constituent, and the mixed rubber constituent of a fluororubber and organic rubber are used. Use of the silicone rubber constituent from a viewpoint of economical efficiency or the mixed rubber constituent of silicone and organic rubber is especially desirable.

[0012] As the silicone and the organic rubber mixture rubber constituent which should be used for the rubber constituent of the outermost layer of drum which constitutes the vulcanization bladder of this invention, this invention persons are Japanese Provisional Publication No. No. 72505 [61 to], and Japanese Japanese Patent Application No. 61-271734th. A number and Japanese Provisional Publication No. 61-175009th A number and Japanese Provisional Publication No. 63-125311st A number and Japanese Provisional Publication No. 61-195810th A number and Japanese Provisional Publication No. 61-100416th All the rubber constituents proposed in the number can be used. Even if fewer [chose and] as a silicone rubber constituent which can be used for the rubber constituent of the outermost layer of drum of the vulcanization bladder used for this invention than the inside of a dimethyl silicone polymer, a methylphenyl silicone polymer, a methyl vinyl silicone polymer, a methylphenyl vinyl silicone polymer, etc., the thing more than a kind is used.

[0013] A reinforcing agent can be added in order to give only the dynamic physical properties which can be equal to use as a vulcanization bladder, the rubber constituent, for example, this silicone rubber constituent, of an outermost layer of drum. What was chosen as this reinforcing agent from organic reinforcing agents, such as inorganic reinforcing agents, such as carbon black, white carbon, a silicic acid anhydride, a water silicic acid, a synthetic silicic acid, an activation calcium carbonate, talc, and an alumina, and high styrene resin, a cumarone indene resin, phenol resin, a lignin, a denaturation melanin resin, and a petroleum resin, is used. Use of silica system reinforcing agents, such as white carbon, a silicic acid anhydride, a water silicic acid, and a synthetic silicic acid, is especially desirable. It can add altogether at the rubber constituent of an outermost layer of drum [for the purpose of chemicals for silicone rubber, such as an antioxidant which is generally used for example, for this silicone rubber constituent in addition to the above-mentioned reinforcing agent, a heat-resistant improver, a vulcanizing agent, and a vulcanization accelerator,].

[0014]

[Function] Steamy interception by the rubber constituent layer which makes organic rubber a principal component, employing efficiently the mold-release characteristic which was excellent in a rubber constituent with small ablation stress, for example, a silicone constituent, by using the

vulcanization bladder with which the ablation stress of the rubber constituent layer and (B) rubber goods which make (A) organic rubber a principal component combined the rubber constituent layer of 0.5 or less kg/cm in this invention. Degradation by the steam which is the fault of a silicone constituent can be prevented, and the endurance of a vulcanization bladder can be raised. Therefore, according to the method of this invention using such a vulcanization bladder, the incidence rate of a molding defective is reduced remarkably and can perform molding vulcanization of rubber goods efficiently.

[0015]

[Example] An example and the example of comparison are given to below, and this invention is more concretely explained to it.

The vulcanization bladder (example article 1) of the multilayer structure which consists of two-layer [of a inner layer and an outer layer] using the rubber constituent shown in example 1 table 1 was produced. That is, the rubber constituent shown in the combination 2 of Table 1 similarly [it is the same with the inner layer of a vulcanization bladder, and] in the rubber constituent which has the mechanical physical properties and hot water resistance which are combination of the component shown in the combination 1 of Table 1 and a component ratio, and are similarly shown in combination 1 is used for the outer layer of a vulcanization bladder, respectively. The vulcanization bladder (example article 1) which carries out a fabricating operation to inner layer 0.1 mm outer layer 4.5 mm according to the layer thickness which Table 2 shows a vulcanization bladder and which is used in the example 1 was produced. Using the vulcanization bladder of the obtained example article 1, molding vulcanization of a pneumatic tire was performed according to the usual method, and the mold-release characteristic and endurance of a vulcanization bladder (example article 1) were evaluated. The mold-release characteristic performed the quality by 2 stage evaluations, made O failure x and showed good in Table 2, respectively. Endurance is shown by % display of the number of times of possible vulcanization of the example article 1 to the number of times of possible vulcanization by the example article 1 of comparison. The test piece of the shape of a with a length width of face [1cm width of face of 15cm] strip of paper is used for exfoliation stress, and it is JIS K 6301-1975. It measured based on the friction test.

The vulcanization bladder (example article 2) was produced like the example article 1 except having set thickness of the inner layer of the vulcanization bladder of the example 2 example article 1 to 1.0 mm. Molding vulcanization of a tire was performed like the example 1 using the obtained example article 2, and, similarly the evaluation result was indicated to Table 2.

[0016]

[Table 1]

表 1

| 重量部 | 配 合 1 | 配 合 2 |
|-----------------------------------|-------|-------|
| ブチルゴム ⁽¹⁾ | 100 | 100 |
| クロロプレンゴム ⁽¹⁾ | 5 | |
| シリコーンゴム ⁽³⁾ | | |
| カーボンブラック ⁽⁴⁾ | 40 | |
| 酸化亜鉛 | 5 | 0.3 |
| ステアリン酸 | 3 | |
| タッキロール201 ⁽⁵⁾ | 5 | |
| ペルオキシド架橋剤 ⁽⁶⁾ | | |
| アロマオイル | 5 | |
| 初期物性 | | |
| 引張強さ(Tb) (kg/cm ²) | 138 | 85 |
| 破断伸び(Bb) (%) | 800 | 630 |
| 硬さ (Hd) | 52 | 50 |
| 耐熱水性 (100℃熱水) | | |
| Tb変化率 (%) | -2 | -43 |
| Bb変化率 (%) | -10 | -32 |
| Hd変化率 (%) | -6 | -12 |

- (1) JSR Butyl268
(2) 昭和ネオプレン ネオプレンW
(3) 東芝シリコーン TSE260-5U
(4) 東芝カーボン 600A
(5) 住友化学工業 アルキルフェノールホルムアルデヒド樹脂
(6) 東芝シリコーン TC-8

[0017]

[Table 2]

表 2

| | 実施例1 | 実施例2 | 比較例1 | 比較例2 |
|--------------------------------|------------------|------------------|------|------|
| 配 合 | 内層 配合1 外層 配合2 | 内層 配合1 外層 配合2 | 配合1 | 配合2 |
| 平均厚さ (mm) | 内層 0.1 外層 4.5 | 内層 1.0 外層 4.5 | 4.5 | 4.5 |
| 離 型 性 | ○ | ○ | × | ○ |
| 耐 久 性 ¹⁾ (Index) | 85 | 98 | 100 | 10 |
| 剥離応力 ²⁾ | 0 | 0 | 8.7 | 0 |

$$1) \frac{\text{テスト品の加硫回数}}{\text{比較例品1の加硫回数}} \times 100$$

2) 長さ15cm幅1cmの短冊状の試験片を使用し、JIS K 6301-1975 はく離試験に準拠して測定した。

[0018] It is combination of the component shown in the combination 1 of example of comparison 1 table 1, and a component ratio, and the vulcanization bladder (example article 1 of comparison) of thickness 4.5 mm was produced using the rubber constituent which has the mechanical physical properties and hot water resistance which are similarly shown in combination 1. Therefore, the example article 1 of comparison is not formed as multilayer structure equipped with the outer layer where exfoliation stress with tire inner liner rubber consists of a rubber constituent layer of 0.5 or less kg/cm. Molding vulcanization of a tire was performed like the example 1 using the obtained example article 1 of comparison, and the evaluation result was shown in Table 2.

It is combination of the component shown in the combination 2 of example of comparison 2 table 1, and a component ratio, and the vulcanization bladder (example article 2 of comparison) of thickness 4.5 mm was produced using the rubber constituent which has the mechanical physical properties and hot water resistance which are similarly shown in combination 2. Therefore, the example article 2 of comparison is not formed as multilayer structure equipped with the inner layer which consists of a rubber constituent which makes organic rubber a principal component. Molding vulcanization of a tire was performed like the example 1 using the obtained example article 2 of comparison, and the evaluation result was shown in Table 2.

[0019] The example article 1 and 2 has a good mold-release characteristic and equal endurance compared with the example article 1 of comparison. On the other hand, although the example article 2 of comparison of a mold-release characteristic is good, endurance is inferior to whether it is ** compared with the example article 1 of comparison, and is not used. The example article 2 of comparison shows that the vulcanization bladder which only used the silicone rubber constituent is not used in respect of endurance.

[0020]

[Effect of the Invention] The vulcanization bladder which the molding vulcanization method of the rubber goods of this invention was formed as multilayer structure which consists of two or more layers, and allotted the layer which intercepts the steam formed from the rubber constituent which makes organic rubber a principal component at the maximum inside as described above, and allotted the high layer of a mold-release characteristic to the maximum outside and which secured a mold-release characteristic and endurance simultaneously is used. Since the bladder for tire vulcanization used for this invention is excellent in a mold-release characteristic with above-mentioned

composition and extremely excellent also in a mechanical strength, thermal resistance, saturated-steam-proof nature, and endurance (2), for this reason the molding defective in which molding vulcanization of rubber goods is possible can do so effects, like the life of (3) vulcanization bladder whose yield hardly occurs but improves notably is long, without using (1) release agent, and, thereby, the molding vulcanization method of the tire concerning this invention can carry out molding vulcanization of rubber goods, such as a tire, efficiently by the low cost.

[Translation done.]